

⑫

**EUROPEAN PATENT APPLICATION**

⑫① Application number: **85100768.2**

⑫② Date of filing: **25.01.85**

⑫① Int. Cl.4: **C 07 C 69/003, C 07 C 69/33,**  
**C 07 C 69/58, C 07 C 67/00,**  
**A 61 K 7/48**

⑫③ Priority: **07.05.84 US 607694**

⑫④ Date of publication of application: **11.12.85**  
**Bulletin 85/50**

⑫④ Designated Contracting States: **BE CH DE FR GB IT LI**  
**NL SE**

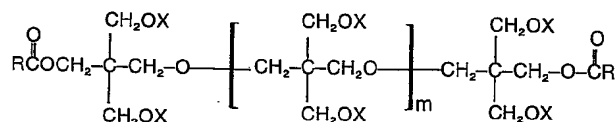
⑫① Applicant: **MIRANOL CHEMICAL COMPANY, INC.,**  
**68 Culver Road P.O. Box 411, Dayton New Jersey (US)**

⑫② Inventor: **Nadolsky, Richard J., Paint Island Spring Road,**  
**Clarksburg New Jersey (US)**  
Inventor: **Fridella, Dominick, 40 Whittier Road, Clark New**  
**Jersey (US)**  
Inventor: **Laryea, Joseph M., 14 Glen Avenue, Old Bridge**  
**New Jersey (US)**

⑫④ Representative: **Baillie, Iain Cameron et al, c/o Ladas &**  
**Parry Isartorplatz 5, D-8000 München 2 (DE)**

⑫④ **Mixtures of oligomers of partially esterified pentaerythritol, their preparation and use.**

⑫⑤ A novel mixture of oligomers obtained of the formula



wherein R is a normal saturated or unsaturated alkyl group of 5 to 17 carbon atoms, X is hydrogen or RC(O), with the proviso that at least one of the X groups is hydrogen and the average value of m is 0 to 5 may be prepared by partial esterification of pentaerythritol with a fatty acid, followed by

acid-catalyzed condensation. Products wherein the average value of m is 1 found use as moisturizers and emollients in cosmetics. Product wherein m is of higher values are of use as lubricants.

MIXTURES OF OLIGOMERS OF PARTIALLY ESTERIFIED  
PENTAERYTHRITOL, THEIR PREPARATION AND USE

BACKGROUND OF THE INVENTION

1. General Subject of the Invention

5           The present invention relates to oligomers of partially esterified pentaerythritol, their production and use in cosmetics and toiletries and as lubricants and corrosion inhibitors.

2. Prior Art

10           Esters of polypentaerythritols have been known for many years. For example, U.S. Patent 2,686,766 (Silverstein et al issued August 17, 1954) describes the use of tripentaerythritol which has been partially esterified with a fatty acid as defoaming agents in synthetic rubber  
15           latex base water emulsion paints. A typical product is obtained by reaction of tripentaerythritol with methyl laurate in the presence of a base.

          U.S. Patent 2,958,706 (Hurwitz et al issued November 1, 1960) describes the substantially complete  
20           esterification of mixture of polypentaerythritol with fatty acids of 4-8 carbon atoms. The products have a hydroxyl value less than 5 and are useful in plasticising polyvinyl chloride.

          U.S. Patent 2,975,152 (Hurwitz et al issued  
25           November 1, 1961) describes the esterification of pentaerythritols and polypentaerythritols to produce plasticisers for polyvinylchloride.

          U.S. Patent 4,421,565 (DiBella issued December 20,

U.S. 607,694

1983) describes a thixotropic agent obtained by reacting a mixture of polypentaerythritols with a fatty acid of 20 to 22 carbon atoms. Reference is, however, made to the possibility of using as the fatty acid, "behenic acid", a commercial mixture of fatty acids consisting predominantly of C<sub>20</sub> and C<sub>22</sub> acids but containing less than 10% C<sub>18</sub> acids.

In commonly assigned co-pending application 574,927 filed on January 30, 1984, there are described partial esters of tripentaerythritol of a fatty acid. These products are soft solids and have moisturizing and emollient properties and are useful in toiletries and cosmetics.

In the acid catalyzed esterification of pentaerythritol using from 0.5 to 2.5 moles of fatty acid per mole of pentaerythritol, we have surprisingly found that after removal of the required amount of water to form partial esters of pentaerythritol further elimination of water occurs readily under the same conditions employed for esterification. This further reaction yields novel condensation products which are apparently oligomers of the pentaerythritol partial esters.

These products differ from those obtained by esterification of polypentaerythritol (described in co-pending application 574,927 filed on January 30, 1984) in that, for a given fatty acid at a given ratio of fatty acid to contained pentaerythritol, the oligomeric products described herein are more liquid than those derived from a polypentaerythritol. Without wishing to be bound by any theory, we believe a possible explanation for this difference may lie in the fact that the products produced in the present case are mixtures of oligomers rather than a single oligomer, and that the distribution of ester groups is more random in the present case than in products made from a polypentaerythritol.

#### SUMMARY OF THE INVENTION

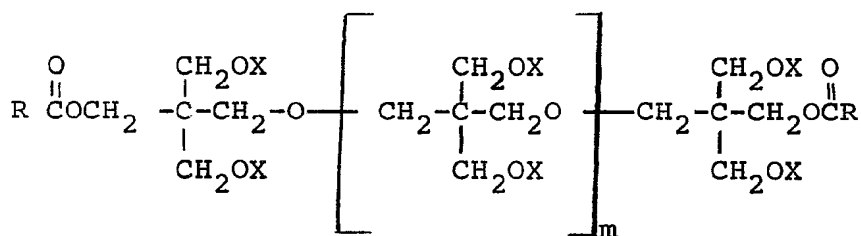
From a first aspect, the present invention provides

a mixture of oligomers of pentaerythritol which has been esterified with from 0.5 to 2.5 moles of a saturated or unsaturated fatty acid of 6 to 18 carbon atoms, for example 12 to 17 carbon atoms preferably 12 to 16 carbon atoms per mole of pentaerythritol wherein said mixture of oligomers contains an average of 2 to 7 partially esterified pentaerythritol units per oligomer chain.

From a second aspect, the present invention provides a process for the production of such oligomers which comprises esterifying pentaerythritol with from 0.5 to 2.5 moles per mole of pentaerythritol of a saturated or unsaturated fatty acid of from 6 to 18 carbon atoms and condensing said partially esterified pentaerythritol so as to remove from 0.5 to 0.85 moles of water per mole of partially esterified pentaerythritol.

It will be appreciated that the number of moles of water removed determines the average chain length of the oligomer produced. Thus, removal of 0.5 moles of water per mole of partially esterified pentaerythritol results in a product wherein the "average" product contains two pentaerythritol residues whereas removal of 0.85 moles of water per mole of partially esterified pentaerythritol results in a product where the "average" product contains seven pentaerythritol residues.

The condensation reaction produces oligomers of a typical formula



wherein R is a normal saturated or unsaturated alkyl group of 5 to 17 carbon atoms, X is hydrogen or RC(O) - with the proviso that at least one of the X groups is hydrogen and

m is an average which is 0 to 5. In any product according to the invention there is a mixture of oligomers of different chain lengths, the distribution of chain length of oligomers about the average chain length typically following a normal distribution.

Particularly preferred compositions according to the present invention are those where the average value of m is 1. That is to say products obtained by the elimination of 0.66 moles of water per mole of partially esterified pentaerythritol. The degree of esterification of the pentaerythritol oligomer is normally in the range 12.5 to 62.5%, preferably in the range 25 to 50%.

Products according to the present invention are prepared by first partially esterifying pentaerythritol with a normal saturated or unsaturated fatty acid of 6 to 18 carbon atoms using from 0.5 to 2.5 moles of fatty acid per mole of pentaerythritol. Typically the fatty acids used are lauric, myristic, palmitic, stearic and oleic acids and mixtures of such acids. The esterification is effected in a suitable solvent that will azeotropically remove the water of reaction and in the presence of a suitable acidic catalyst. Reactions normally are run at temperatures of 150-200°C. Suitable solvents are benzene, toluene, xylene or other solvent that will form an azeotrope with water and allow for achieving a reaction temperature in the range given above. Suitable catalysts are p-toluenesulfonic acid, stannous octoate, or other sufficiently thermally stable Lewis or Bronsted acid. We have, however, found that the partial esterification can in some cases also be effected without the need for a carrier-solvent for removal of water. If a high equivalent weight acid such as p-toluene sulfonic acid is used as catalyst, an excess of this above the amount recorded for catalyst with solvent present will enable the use of a solvent to be avoided. As an alternative, one may use a catalytic amount of a lower equivalent weight acid such

as sulfuric acid. Other convenient acids such as methane sulfonic or a mixture of methane sulfonic and hypophosphorous acids may, however, be used to effect the catalysis. The partially esterified pentaerythritol is then condensed to  
5 form the oligomers by continued treatment under the same conditions as those used for the partial esterification.

The oligomeric partial esters of pentaerythritol where the average value of  $m$  is 1 and the fatty acid is of 12 to 18 preferably 12 to 16 carbon atoms are particularly  
10 useful as moisturizers and emollients in cream and lotion formulations. In addition, the oligomeric products, being liquid are easy to work with. The oligomeric products are also useful in lipstick bases and bar soaps. We have found that such oligomers have surprisingly  
15 beneficial moisturization and emollient properties. The oligomer mixtures of the present invention especially those of esters of fatty acids of 6-12 carbon atoms also possess lubricating and corrosion-inhibiting properties. Such compositions may be water-or oil-based and typically  
20 contain 0.5 to 20%, more commonly 1-10% by weight of the oligomer mixture of the present invention. The corrosion inhibiting compositions are useful in providing protection against acids, alkalis, salts and oxidants.

Cream and lotion formulations normally comprise  
25 emulsifiers. Suitable emulsifiers include amine salts of fatty acids of 12 to 20 carbon atoms, for example, alkanolamine salts (e.g. triethanolamine salts) of lauric, myristic, stearic and palmitic acids, mono esters of glycerol with fatty acids of 12 to 20 carbon atoms, such  
30 as glycerol monostearate, poly alkoxylated fatty alcohols of 12 to 20 carbon atoms, such as ethoxylates, propoxylates and oleyl alcohol and poly alkoxylate esters such as poly ethoxylates and polypropoxylates) of fatty acids 12 to 20 carbon atoms having from 1 to 20 alkylene oxide units.  
35 Such compositions may also contain humectants such as glycerol, sorbitol and  $C_2-C_4$  alkylene glycols, such as

propylene glycol.

Both creams and lotions incorporating the oligomer mixtures of the invention contain substantial quantities of water. The exact physical composition depending upon the ratio of emulsifier to water. We have found that compositions of the present invention required the presence of a lower amount of emulsifier than do prior art moisturizing compositions to ensure a stable cream form of the composition. Typically, skin lotions according to the present invention contain from 65 to 85 percent by weight water whereas creams contain less than 50 percent by weight water.

Such compositions may also contain further components such as emollients. For example, acetylated lanolin alcohols, isopropylmyristate or isopropyl palmitate or mineral oils may be used for this purpose, particularly in moisturizing lotions. However, in view of the emollient properties of the oligomers of the present invention the amount of such emollients present in the compositions of the present invention will be substantially reduced as compared to prior art compounds. For example, the amount of such emollients present in moisturizing creams according to the present invention may be reduced to 5 percent by weight or less.

Other components may also be employed as convenient, for example, stearyl or other fatty alcohols as secondary emulsifiers, materials such as petrolatum and thickeners such as colloidal magnesium aluminum silicate. In particular, it should be noted that the application of compositions according to the present invention is not confined to preparations which are purely moisturizing in function (such as moisturizing creams and lotions) but also find use in other cosmetic preparations where the moisturizing properties of the composition are important such as foundation creams and eyeshadows. Compositions according to the invention which are intended

for use in these roles will have the conventional additives used in such compositions, such as cosmetically acceptable pigments.

For example, lipstick, bar soap and makeup foundation compositions may be formulated in accordance with the present invention. Typically, a lipstick composition comprises waxes such as beeswax, carnauba wax and candellila wax together with an emollient such as mineral oil and liquid lanolin base. It also contains pigment normally milled in a liquid base and an opacifier such as titanium dioxide. Foundation makeups typically contain a self emulsifying wax, an emollient such as isopropyl stearate, propylene glycol dipelargonate and opacifiers and pigments such as kaolin and titanium dioxide.

Compositions using the oligomer mixture of the invention typically contain from 2 to 10 percent preferably 2.5 to 5 percent by weight of the oligomers of partially esterified pentaerythritol.

The invention is illustrated by the following Examples in which all percentages are by weight.

Example 1:

To a flask equipped with thermometer, mechanical stirrer, reflux condenser and Dean-Stark trap charge a blend (71/29) of lauric/myristic acid (277.0g, 1.33 moles), xylene (60g) and p-toluene-sulfonic acid (1.7g). Heat, with stirring, to 60°C. and bubble a slow stream of nitrogen through the mixture during the entire course of the reaction. At 60°C., add pentaerythritol (136.0g, 1.0 mole) and heat to 190-195°C. over a period of about 1 hour. Care must be taken not to increase temperature at too fast a rate since the pentaerythritol begins to sublime at about 180° by proper control of the rate of temperature increase this sublimation can essentially be avoided and the theoretical amount of water (24 ml, 1.33 moles) collected below 190°C.

When the desired temperature is achieved, continue cooking



to remove water resulting in ether formation. When an additional 12 ml of water has been removed, the reaction mixture is cooled below 100°C. and the catalyst is neutralized by adding 2.0g of 25% methanolic sodium methoxide. Methanol and xylene are then stripped off under vacuum at a maximum temperature of 200°C. The product is cooled to 80°C. and poured from the flask. After cooling to room temperature, the product is hazy, viscous, yellow liquid.

10 Example 2:

A product is made by the same procedure as example 1, except the mole ratio of lauric/myristic acid to pentaerythritol is 1.66 to 1.0. This product is also a hazy, viscous liquid.

15 Example 3:

A product is made by the procedure of example 1 using a 1.0: 1.0 mole ratio of lauric/myristic acid to pentaerythritol. The product is a hazy, viscous liquid.

Example 4:

20 A product is made by the procedure of example 1, except 85% stearic acid is used instead of lauric/myristic acid blend. This product is a hard, cream-colored solid.

Example 5:

25 A product is made by the procedure of example 1 substituting lauric acid for the lauric/myristic acid blend. This product is a hazy, viscous liquid.

Example 6:

30 A product is made by the procedure of example 1 using oleic acid instead of the lauric/myristic acid blend. The product is a dark liquid.

Example 7:

35 A product is made by the procedure of example 1, except that xylene is excluded and sulfuric acid (1.7g) is used in place of p-toluenesulfonic acid. The product is a hazy, viscous liquid whose performance in the various formulations listed is indistinguishable from that of product made

according to example 1.

Example 8: CLEANSING CREAM

I.

	<u>A</u>	<u>B</u>
Product from Example 1 (batch 1)	4.0	-
5 Tripentaerythritol tetra-Laurate/Myristate	-	4.0
Mineral Oil	10.0	10.0
Cerasynt SD <sup>1</sup> (Van Dyk & Co.)	5.0	5.0
Stearyl Alcohol	0.5	0.5
Cetyl Alcohol	0.5	0.5

10 II.

Water	71.2	71.2
Veegum HV <sup>2</sup> (R.T. Vanderbilt)	0.5	0.5
Xanthan Gum (Kelco)	0.8	0.8

III.

15 MIRANOL C2M-SF CONC.	7.5	7.5
-------------------------	-----	-----

1. Glyceryl monostearate
2. Colloidal magnesium aluminum silicate thickener

20 Procedure: Mixture I was heated to 75°C. Mixture II was heated with stirring to 80°C. until uniform. With agitation, II was added to I and III then added. Agitation was continued until uniform and the composition was then allowed to cool.

30 EVALUATION: A panel of four was asked to judge these products on the basis of texture, absorbability and feel on the skin. A was chosen over B (4:0)

Example 9: MOISTURIZING LOTION

I	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
35 Product from Example 1 (batch 1)	5.0	-	-	-	-
Product from Example 1 (batch 2)	-	-	-	5.0	-
Tripentaerythritol tetra-Laurate/myristate	-	5.0	-	-	-
40 Glycerin	-	-	5.0	-	-
Super Sterol Ester (Croda)	-	-	-	-	5.0

Example 9 (con't)

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Arlacel 165 <sup>1</sup> (ICI Americas)	6.0	6.0	6.0	6.0	6.0
Mineral Oil	3.0	3.0	3.0	3.0	3.0
5 Stearic Acid	2.0	2.0	2.0	2.0	2.0
Acetol <sup>2</sup> (Emery Industries)	1.0	1.0	1.0	1.0	1.0

II

Water	78.5	78.5	78.5	78.5	78.5
Veegum HV	0.5	0.5	0.5	0.5	0.5
10 Propylene Glycol	3.5	3.5	3.5	3.5	3.5
Triethanolamine	0.5	0.5	0.5	0.5	0.5

1. Glycerol monostearate and polyoxyethylene stearate
2. Acetylated lanolin alcohols

PROCEDURE: Mixtures I and II were heated separately to 75°C.

- 15 Mixture II was added to mixture I with agitation. Mixing was continued until uniform, the formulations were then allowed to cool.

EVALUATION: In terms of the performance criteria cited above, a panel of five gave the following ratings:

- 20 A>D>B>>C, E

Example 10:

NIGHT CREAM

I	<u>A</u>	<u>B</u>	<u>C</u>
Product from Example 1 (batch 1)	4.0	-	-
Product from Example 1 (batch 2)	-	-	4.0
25 Tripentaerythritol tetra-Laurate/Myristate	-	4.0	-
Mineral Oil	25.0	25.0	25.0
Arlacel 165	6.0	6.0	6.0
Isopropyl Myristate	5.0	5.0	5.0
30 Cetyl Alcohol	0.5	0.5	0.5

II

Water	48.7	48.7	48.7
Carbopol 934 <sup>1</sup> -3% soln. (B.F. Goodrich)	5.0	5.0	5.0

Example 10 (con't)

	<u>A</u>	<u>B</u>	<u>C</u>
Propylene Glycol	5.0	5.0	5.0

III

5	Triethanolamine	0.8	0.8	0.8
---	-----------------	-----	-----	-----

1. Polyacrylic Acid

PROCEDURE: Mixture I and II were heated separately to 75°C. Mixture II was then added with agitation to mixture I and III added thereto. Agitation was continued until uniform then the product was allowed to cool.

10

EVALUATION: On the basis of the previously-cited performance characteristics, a panel of five gave the following ratings:

15

A, C > B

Example 11: MOISTURIZING CREAM

	<u>A</u>	<u>B</u>	<u>C</u>	
I				
	Product from Example 1 (batch 1)	4.0	-	-
	Product from Example 1 (batch 2)	-	4.0	-
20	Glycerin	-	-	4.0
	Mineral Oil	3.5	3.5	3.5
	Isopropyl Myristate	2.0	2.0	2.0
	Propylene Glycol Dipelargonate	1.0	1.0	1.0
	Arlacel 165	5.0	5.0	5.0
25	Beeswax	2.0	2.0	2.0
	Stearic Acid	1.0	1.0	1.0
	Stearyl Alcohol	0.5	0.5	0.5
	Dow Corning Fluid 200	0.5	0.5	0.5
	II	<u>A</u>	<u>B</u>	<u>C</u>
30	Water	68.7	68.7	68.7
	Propylene Glycol	3.5	3.5	3.5
	Carbopol 934 - 3% soln.	7.5	7.5	7.5
	III			
	Triethanolamine	0.8	0.8	0.8

5      PROCEDURE:      Mixtures I and II were heated separately to 75°C. With agitation, mixture II was added to mixture I and component III then added thereto. Agitation was continued until uniform and the product allowed to cool.

EVALUATION:      On the basis of previously cited performance criteria, a panel of five gave the following ratings:

A > B (slightly) >> C

10	<u>Example 12:</u>	<u>MOISTURIZING LOTION</u>			
	I		<u>A</u>	<u>B</u>	<u>C</u>
	Product from Example 3		5.0	-	-
	Product from Example 2		-	5.0	-
	Product from Example 1 (batch 1)		-	-	5.0
15	Arlacel 165		6.0	6.0	6.0
	Mineral Oil		3.0	3.0	3.0
	Stearic Acid		2.0	2.0	2.0
	Acetol		1.0	1.0	1.0
	II				
20	Water		78.5	78.5	78.5
	Veegum HV		0.5	0.5	0.5
	Propylene Glycol		3.5	3.5	3.5
	Triethanolamine		0.5	0.5	0.5

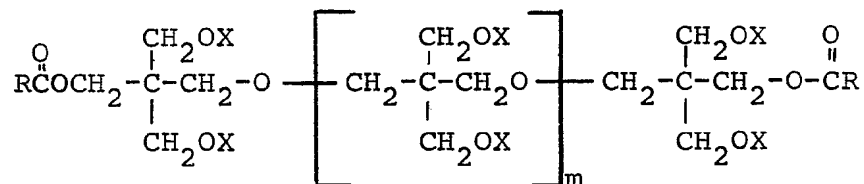
25      PROCEDURE:      Mixtures I and II were heated separately to 75°C. With agitation, mixture II was added to mixture I. Mixing was continued until uniform and the composition then allowed to cool

EVALUATION:      Using previously cited criteria, a panel of four gave the following ratings:

30                      C > B (slightly) > A

C L A I M S

1. A mixture of oligomers of the formula:



wherein R is a normal saturated or unsaturated alkyl group of 5 to 17 carbon atoms, X is hydrogen or RC(O), with the proviso that at least one of the X groups is hydrogen and the average value of m is 0 to 5.

2. A mixture of oligomers according to claim 1, wherein the average value of m is 1.
3. A mixture of oligomers according to claim 2, wherein an average of from 3 to 5 X groups are hydrogen.
4. A mixture of oligomers according to either of the preceding claims, wherein R is a normal saturated or unsaturated alkyl group of 12 to 16 carbon atoms.
5. A mixture of oligomers according to claim 4, wherein RCO is a lauroyl, myristoyl, palmitoyl, stearoyl or oleoyl group.
6. A process for preparing a mixture of oligomers according to claim 1, which comprises esterifying pentaerythritol with from 0.5 to 2.5 moles of a normal saturated or unsaturated fatty acid of from 6 to 18 carbon atoms and subjecting the partial ester product thereof to acid-catalyzed condensation to extract from 0.5 to 0.85 moles of water per mole of pentaerythritol.
7. A process according to claim 6, wherein the condensation is effected to extract about 0.66 moles of water per mole of pentaerythritol.
8. A process according to either of claims 6 and 7, wherein the partial esterification is effected with from 1 to 2 moles per mole of pentaerythritol of an acid selected from lauric, myristic, palmitic, stearic and oleic acids and mixtures thereof.
9. A composition suitable for topical application to the

skin which comprises an effective moisturizing or emollient amount of an oligomer mixture of partially esterified pentaerythritol as defined in any one of claims 1 to 5.

10. A composition according to claim 9, which further contains a cosmetically-acceptable emulsifier.

11. A composition according to claim 10, wherein said emulsifier is selected from the group consisting of amine salts of fatty acids, monoesters of glycerol with fatty acid, fatty alcohols of 12 to 20 carbon atoms which are optionally polyalkoxylated and polyalkoxylated esters of fatty acids of 12 to 20 carbon atoms.

12. A composition according to claim 11, wherein said oligomer mixture of partially esterified pentaerythritol is an ester where from 0.5 to 2.5 of the hydroxy groups of the pentaerythritol have been esterified with a fatty acid selected from lauric, myristic, stearic, palmitic and oleic acids.

13. A composition according to claim 12, which further comprises an emollient.

14. A composition according to claim 10, which further comprises an emollient selected from the group comprising acetylated lanolin alcohols, isopropylmyristate and isopropylpalmitate and mineral oil.



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 85100768.2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	PATENT ABSTRACTS OF JAPAN, unexamined applications, section C, vol. 3, no. 128(-62), October 24, 1979  THE PATENT OFFICE JAPANESE GOVERNMENT page 23 C 62  * Kokai-no. 54-106 415 (NISSHIN SEIYU K.K.) *  --	1-5,9	C 07 C 69/003 C 07 C 69/33 C 07 C 69/58 C 07 C 67/00 A 61 K 7/48
X	US - A - 3 670 013 (R.T. LEIBFRIED)  * Example; claims *  --	1,6	
A	EP - A2 - 0 100 652 (NUODEX INC.)  * Claims *	1,6	
D,A	& US-A-4 421 565  --		TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	DE - B - 1 200 795 (ROHM & HAAS)  * Claims *	1,6	C 07 C 69/00
D,A	& US-A-2 958 706  -----		
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 28-06-1985	Examiner HOFBAUER
<b>CATEGORY OF CITED DOCUMENTS</b>  X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document			

